Chemical Analysis of Ultra-Thin Films: Understanding Chemical Changes as a Result of EUV Irradiation

Idriss Blakey, Kirsten J. Lawrie, Kevin S. Jack, Andrew K. Whittaker

The University of Queensland, Australian Institute for Bioengineering and Nanotechnology, Centre for Advanced Imaging, and Centre for Microscopy and Microanalysis St Lucia, Brisbane, 4072, Australia

Introduction

- As feature sizes decrease, so does the resist layer thickness.
  - Film thicknesses of <50 nm will soon become common.
- **Ultra-thin films can have very different properties *cf.* bulk.**
  - E.g. the glass transition temperature can either decrease or increase depending on the interaction with the substrate.
- These changes can significantly influence chemical reactions.
  - This could be **potentially catastrophic for lithography**.
- For 193 nm irradiation of PMMA, we have shown that the rate of change of film thickness and refractive index as a function of dose differs significantly for thin films (Fig. 1).

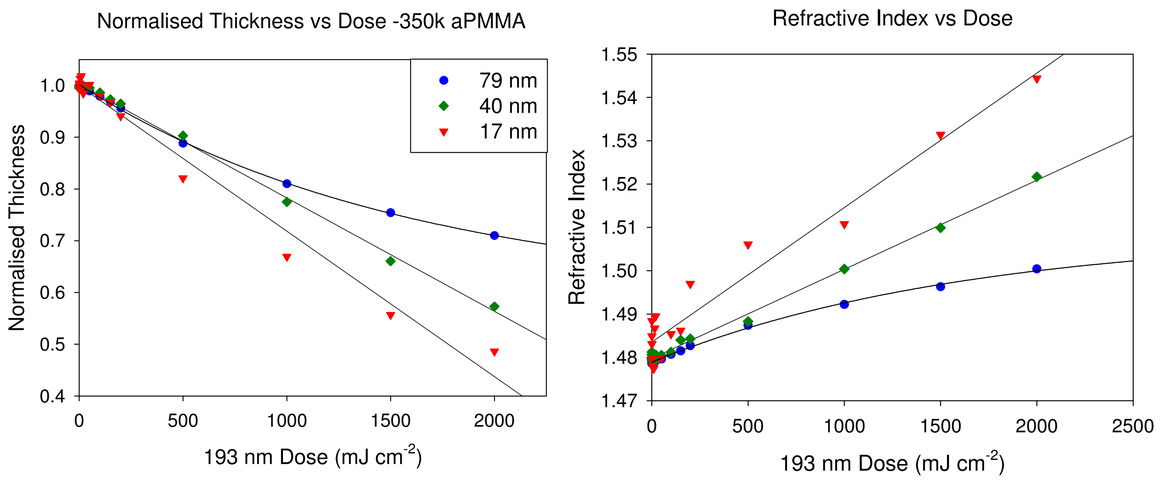

Fig 1. Change in (left) thickness and (right) refractive index of thin films as a function of 193 nm dose.

- Monitoring chemical reactions in thin films can be extremely challenging for traditional chemical metrology techniques.
- **Here we report on techniques for monitoring of chemical changes in ultra-thin films,** using non-CAR resists as examples, but the techniques are also equally suited to studying chemically amplified resists.

Grazing Angle Attenuated Total Reflectance (GATR) -FTIR

- Standard infrared (IR) methods:
  - Excellent for monitoring chemical changes .
  - Not sensitive enough for analysis of thin films.
- **GATR** has a sample geometry (Fig. 2) that r**esults in high sensitivity, allowing IR spectra of very thin films to be measured (monolayer – 50 nm)**
- Fig. 3 shows loss of SO_2 in a 20 nm polysulfone film as a function of irradiation with 92 eV photons[1].

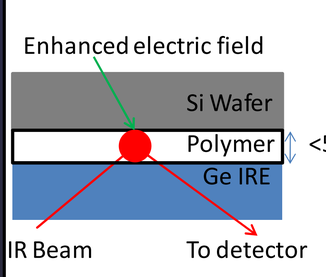

Fig 2. GATR FTIR sample configuration and beam path. Enhanced electric field (100x) occurs in thin (<50 nm) polymer film that is sandwiched between a high refractive index (RI) Si wafer and high RI Ge IRE.

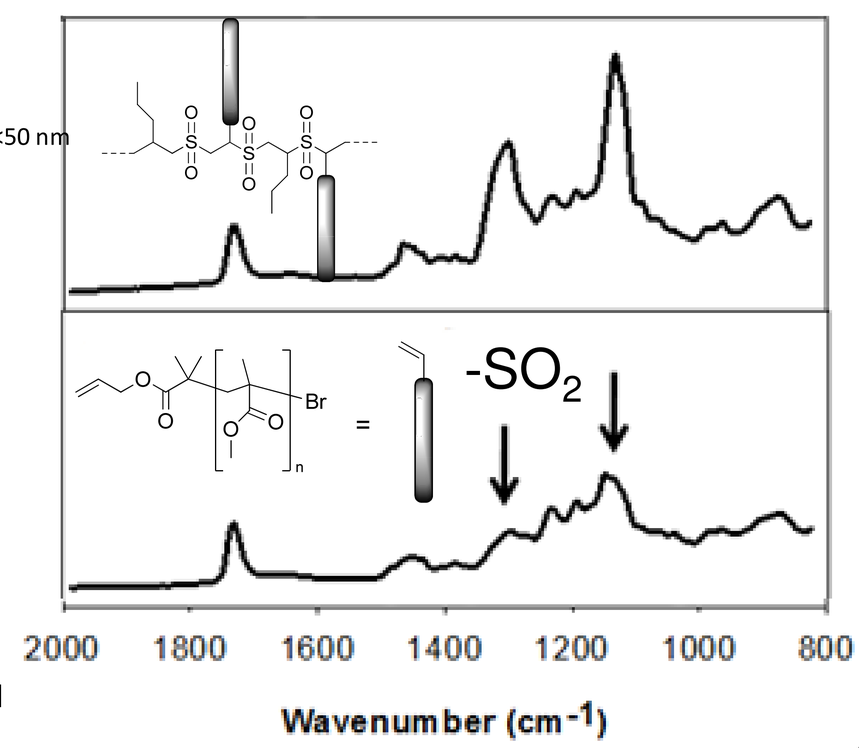

Fig 3. GATR FTIR spectra of (top) unirradiated polymer and (bottom) irradiated polymer, where loss of SO_2 can be observed.

X-ray Photoelectron Spectroscopy (XPS)

- XPS is a surface sensitive technique that can follow chemical changes in the top ~10 nm of polymer films.
  - Allows **determination of elemental composition.**
  - In-depth analysis gives information on **functional groups.**
  - In situ irradiation with X-rays is analogous to EUV.
- Fig. 4 shows the changes that occur in 20 nm thick poly(pentene sulfone) as a result of irradiation with 700 eV Synchrotron X-rays.[2]
  - A decrease in SO_2 is observed, but also appearance of a sulfide based side product was also observed.

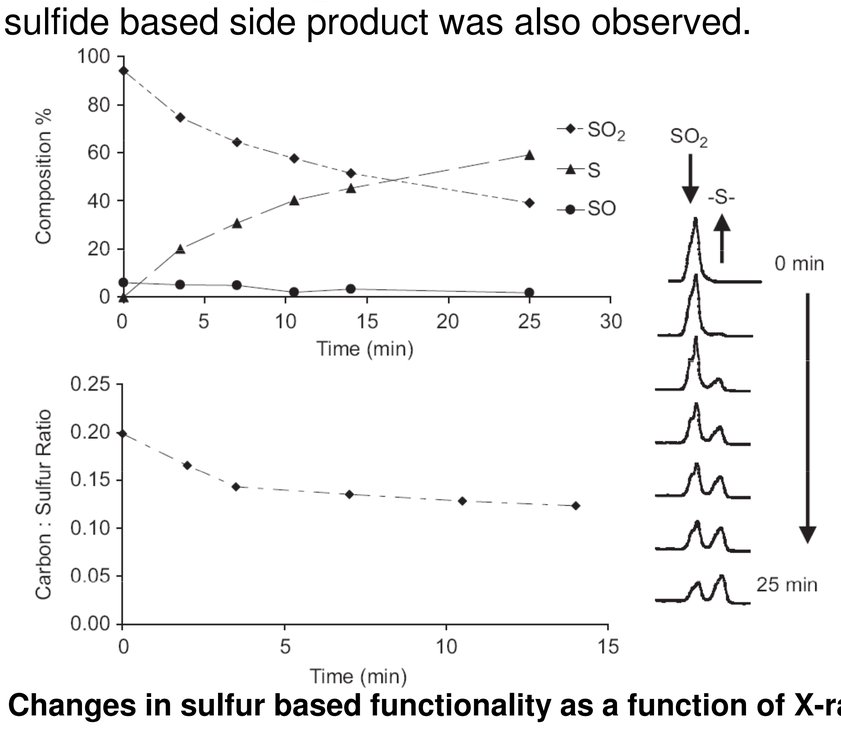

Fig 4. Changes in sulfur based functionality as a function of X-ray dose.

Near Edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy

- NEXAFS is similar to XPS in its surface sensitivity.
  - Provides direct information on bonding, e.g. **distinguishes between σ and π bonding.**
- Fig. 5 shows O and C K-edge NEXAFS spectra for **20 nm thick** polymer films that are untreated, heat treated and irradiated with 650 eV X-rays.
  - Changes of carbonyl based functional groups can be seen.

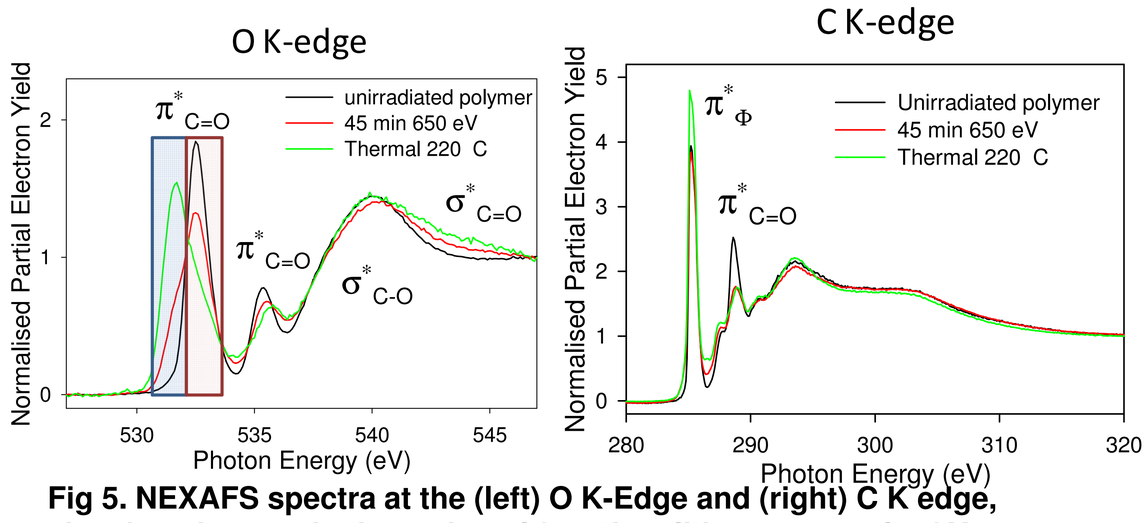

Fig 5. NEXAFS spectra at the (left) O K-Edge and (right) C K edge, showing changes in the carbonyl functionalities as a result of X-ray irradiation or heating.

Summary/Conclusions

- Three powerful techniques for monitoring chemical changes in thin polymer films (monolayer - 50 nm) have been discussed.
- Examples have been given for monitoring chemical changes in non-CAR resists, but there is **significant scope to understand the effect of reducing film thickness on chemical changes that occur in chemically amplified resists.**

References

1. K. J. Lawrie, I. Blakey, J. P. Blinco, H. H. Cheng, R. Gronheid, K. S. Jack, I. Pollentier, M. J. Leeson, T. R. Younkin, A. K. Whittaker, *J. Mater. Chem.* ***2011, 21, 5629.***
2. K. Lawrie, I. Blakey, J. Blinco, R. Gronheid, K. Jack, I. Pollentier, M. J. Leeson, T. R. Younkin, A. K. Whittaker, *Radiat. Phys. Chem.* ***2011, 80, 236.***

ACKNOWLEDGEMENTS

The authors would like to thank, the Australian Research Council (Project ID LE0775684, DP0878615 and DP1094205), Smart State Innovation Building Fund for funding and the ANFF-Q for use of instrumentation.